



Influence of alkali carbonates on benzyl phenyl ether cleavage pathways in superheated water

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ABSTRACT

Benzyl phenyl ether conversion in superheated water yields a broad product distribution. In addition to the hydrolysis products, phenol and benzyl alcohol, a large amount of consecutive products are formed depending on the operating conditions. The influence of Li_2CO_3 , Na_2CO_3 , and K_2CO_3 on these reactions is explored between 270 and 370 °C. It is shown that high selectivity towards hydrolysis can be achieved at low temperatures and short reaction times. At higher severities the yields of phenol and especially benzyl alcohol decrease and higher molecular weight compounds are formed by consecutive reactions. Alkali carbonates effect this distribution by decreasing the concentration of protons in the system and by providing and enhancing parallel and secondary reaction mechanisms. The yields of toluene, 2 and 4-benzyl phenol are strongly enhanced in the presence of an alkali carbonate, by formation of a cation–BPE adduct in which the ether bond is strongly polarized.

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1. Introduction

Lignin and coal constitute a large fraction of the organic matter and are used to cover a significant fraction of present day energy usage (i.e., 10% and 25%, respectively). Both are mostly employed as direct fuel or are gasified to hydrogen or synthesis gas, despite the potential to utilize structural motifs as clean energy carriers or chemicals. This is not possible to date, as the recombination of the fragments after deconstruction is quite fast once a higher conversion is achieved. In order to realize new approaches to deconstruct lignin and coal, the chemistry of deconstructing the polymers and the structural organic motifs has to be understood in greater detail.

Phenoxy linkages are important structural bonds in both low rank coal and lignin [1]. For example, in hardwood, 60% of phenolic monomers are linked by aryl–alkyl (α - and β -O4) ether bonds [2]. Unlike the aryl–aryl type ether bond, as in diphenyl ether (DPE), aryl–alkyl ethers can be cleaved in subcritical water [3,4].

In order to explore the potential catalytic chemistry we have applied benzyl phenyl ether (BPE) as model compound to represent the α -O4 ether bond in lignin and coal. This compound contains a weak ether bond of 234 kJ/mol and belongs to the most thermo-labile compounds in lignin and low rank coal [1].

In the following sections, the effect of alkali carbonates, common additives in biomass conversion, on the reaction pathways of BPE in superheated water will be presented. We have chosen this reaction medium not only due to its green nature but also due to its unique solvating and transportation properties, which can easily be adjusted. As a result of these beneficial characteristics superheated water has recently found broad application in biomass conversion and coal extraction. It was shown that it exceeds the efficiency of supercritical toluene due to its ability to participate in hydrolysis of ether linkages in coal [5].

Literature suggests the conversion of α -O4 ethers in superheated water to proceed via parallel hydrolysis and pyrolysis pathways [4,6,7]. Examples for the most commonly proposed BPE pyrolysis and hydrolysis pathways, as well as an excerpt of possible products deriving from the hydrothermal treatment of BPE are summarized in Fig. 1.

Hydrolysis is a heterolytic pathway leading to the formation of benzyl alcohol and phenol (Reaction 1.1) [4]. If the ether bond is cleaved homolytically as in a pyrolysis reaction, a phenoxy and a benzyl radical are generated. Being highly reactive, they may react with hydrogen radicals to produce phenol and toluene (2.1), recombine among themselves (2.2), and react with BPE (3) or the hydrolysis products [9,10]. In these latter cases, dimers, trimers, and higher molecular weight compounds would be formed. The products presented in Fig. 1 are only exemplary and many other consecutive products can be formed. In contrast to the other products formed by hydrothermally treated BPE, toluene formation is almost always described by a pyrolysis

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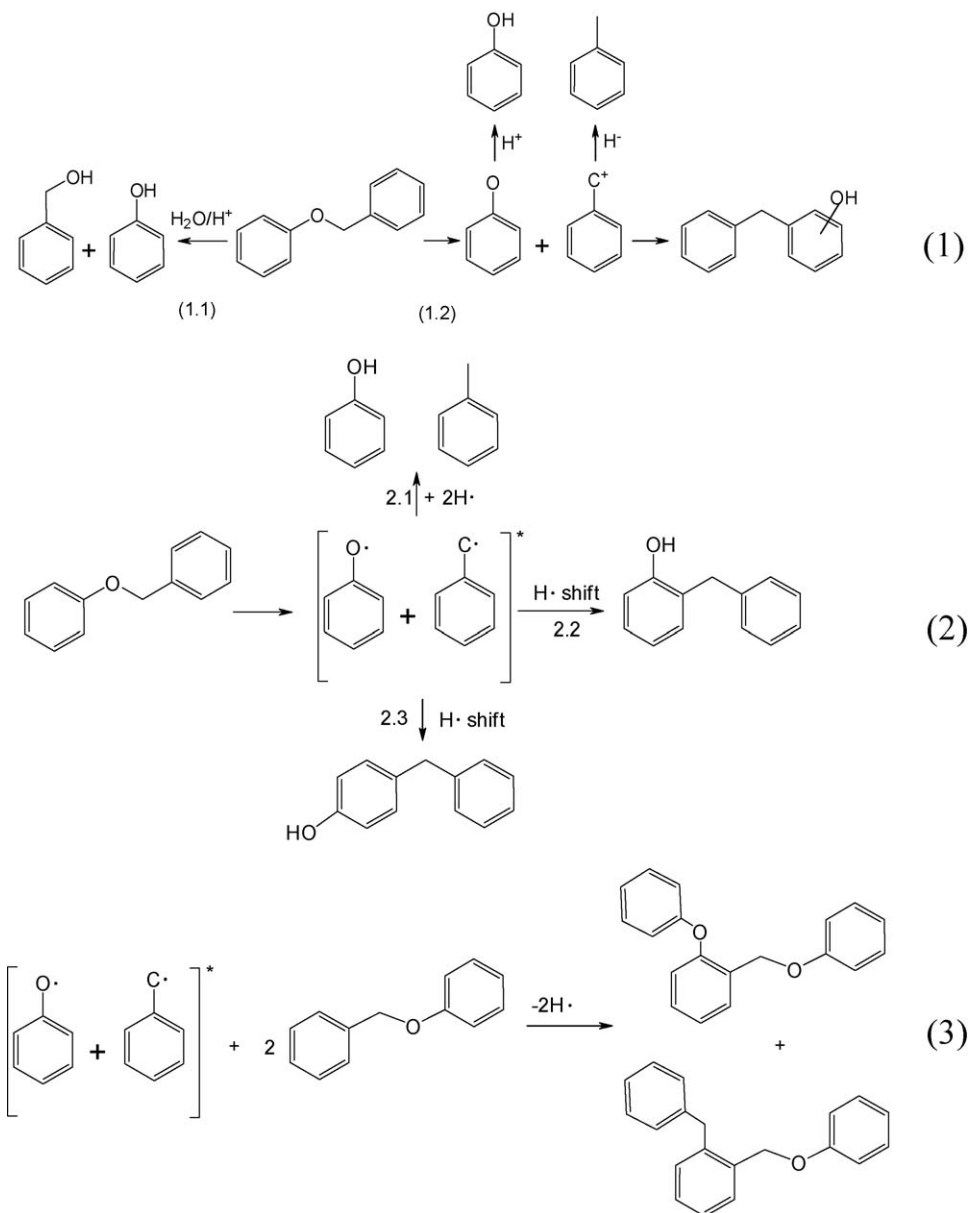


Fig. 1. Ionic and radical mechanism pathways with possible recombination products according to refs. [4,5].

mechanism [4,9,11]. Katritzky et al., on the other hand, stated that toluene forms via an ionic mechanism, in which the benzyl cation, generated from heterolytic cleavage of the BPE ether bond, either attacks phenol or abstracts a hydride to form 2 and 4- benzyl phenol and toluene respectively as shown in reaction (1.2) in Fig. 1 [8].

It has been shown that reaction pathways can be shifted towards hydrolysis by enhancing the ionic properties of the aqueous phase by adding salts or by increasing the phase density when reacting α -O4 ethers in superheated water [4,12]. Yokoyama et al. reported that an increased density not only favors hydrolysis, but also accelerates reactions such as hydrogen abstraction and radical recombination [4].

The presented study gives insight on how the addition of alkali carbonates interacts with reaction conditions to effect reaction pathways of BPE conversion in superheated water. It is shown that the formation of 2-benzyl phenol, 4-benzyl phenol and especially toluene proceeds via an ionic reaction mechanism contrary to the radical mechanism, which is most frequently postulated.

2. Experimental

The experiments were carried out in stainless steel tube autoclaves at temperatures from 270 to 370 °C with reactant mixture density of 0.9 g/cm³, consisting of 3 wt.% of the alkali carbonate (Li₂CO₃, Sigma, 99.0%; Na₂CO₃, Sigma, 99.5%; K₂CO₃, Sigma, 99.0%) and 5 wt.% BPE (Aldrich, 98%) in an appropriate amount of water. The density was adjusted by applying the appropriate amount of water. The reactors were set in a preheated alumina block, which was tumbled to ensure sufficient mixing. An initial heat up time of 30 min was deducted from the time the reaction mixture was set into the preheated aluminum block. This is the 'reaction time' used in all figures. Deductions of conversions in this interval were not made in the present case. After the reaction, the autoclaves were quenched to room temperature with water. The mixtures of reactants and products (gas-phase products were verified to be as few as negligible) were diluted with acetone to a volume of 50 ml. The reaction products were identified by GC/MS and quantified by GC/FID-analysis using a Shimadzu GC/MS-QP 20105 gas chromatograph-mass spectrometer (column: HP-5,

cross linked 5% PhME siloxane, 30m × 0.32 mm × 0.25 μm). The concentrations of the reactant BPE as well as the products benzene, toluene, phenol, benzyl alcohol, 2- and 4-benzylphenol were determined by calibrating the peak areas with acetone solutions of known concentrations of these compounds.

Laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF) was measured to detect the formed high molecular weight compounds. The mass spectra were recorded using a Bruker Biflex III MALDI-TOF mass spectrometer equipped with a N₂ laser ($\nu = 337$ nm) operating at a pulse rate of 3 Hz. The ions were accelerated with pulsed ion extraction after delay of 50 ns by a voltage of 28.5 kV. The analyzer was operated in reflection mode, and the ions were detected using a micro channel plate detector. Prior to measurement the mass spectrometer was calibrated with a polystyrene standard.

3. Results

In the absence of alkali carbonates, BPE is fully converted after only 5 min at temperatures of 350 and above (see Fig. 2). At 320 °C, conversion has reached 96% after 30 min, while at 270 °C; 240 min are necessary for the conversion to attain 91%.

Fig. 3 shows the effect of the alkali carbonates on BPE conversion from 270 to 350 °C for a reaction time of 60 min. Up to 320 °C, BPE conversion is considerably reduced by the presence of the salts. Beyond this temperature the conversion is 100% in all cases. It should be noted that the inhibiting effect of the carbonates decreases in the sequence $\text{Li}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{K}_2\text{CO}_3$, which corresponds to the sequence of molar concentrations applied.

Table 1 summarizes the products detected for the reaction of BPE at 270 °C after 60 min reaction time without a carbonate added. To better account for mass balance, yields are given in mol C%. At these conditions BPE is converted to 63%. Phenol and benzyl alcohol, however, were produced with a total yield of 40 mol C%. Toluene, the dimers (diphenyl carbinol, 2-benzyl phenol and 4-benzyl phenol) and the trimers (1-benzyl-2-phenoxy-methyl-benzene and 1-phenoxy-4-phenoxy-methyl-benzene) only appeared in low concentrations at 270 °C. Higher molecular weight compounds, which are preferably formed at higher temperatures and longer reaction times, were not detected via GC/MS due to their high boiling points. While their formation was confirmed by LDI-TOF/MS measurements (see Fig. 4), quantification was not possible, so that these products are accounted in the carbon balance as “high molecular weight products”. Molecular weights of these products range up to 617 indicating the formation of oligomers containing up to six benzyl units.

The product distribution of the reaction without addition of carbonates is plotted against the temperature in Fig. 5. The amounts of directly measured reactant and the GC/MS detected products up to trimers decreased with increasing reaction temperature. After the reaction, all products were in the liquid phase and the formation of gaseous products was negligible. The results indicate that with increasing reaction temperature an increasing fraction of the reacted products are too heavy to be detected by the GC/MS. It is remarkable that already at 270 °C approximately 20% of the reactants forms high molecular weight components.

Fig. 6 shows the main product distribution as a function of time on stream at 320 °C without alkali carbonate. The term “secondary

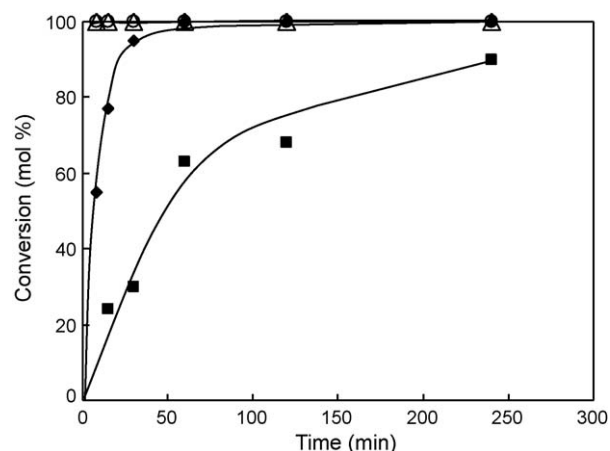


Fig. 2. BPE conversion with reaction time in the absence of base additive at different temperatures: (■) 270 °C; (◆) 320 °C; (△) 350 °C and (○) 370 °C.

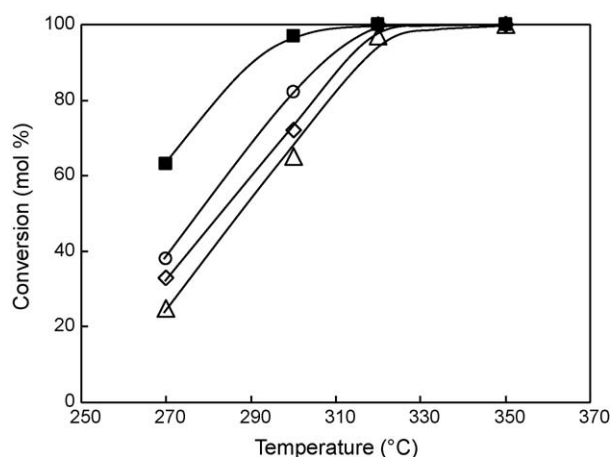


Fig. 3. Influence of addition of different alkali carbonates on BPE conversion after reaction for 60 min at a temperature range of 270–350 °C. (■) no carbonate; (△) Li_2CO_3 ; (◇) Na_2CO_3 and (○) K_2CO_3 .

products” summarizes the GC detectable dimeric and trimeric products. At 320 °C the yields of the hydrolysis products, i.e., phenol and benzyl alcohol, reach a maximum after 30 min reaction time and then decrease, while the secondary reaction products increase and the toluene yield is stable. A comparison of the yields of the hydrolysis products after 60 min at 270 °C (Table 1) and 320 °C (Fig. 6) shows that the temperature increase has an enhancing effect on hydrolysis. However, phenol and benzyl alcohol were not detected in equivalent amounts, when performing the reaction at 320 °C, as would have been expected from a chemical stoichiometric ratio of unity for the hydrolysis reaction. Especially, the lower concentration of benzyl alcohol and the higher concentration of the secondary products illustrate the high reactivity of benzyl alcohol. Note that at this point the time required for heating the autoclaves leaves more time for secondary reactions and causes the offset of the secondary products from the expected value of zero when extrapolating to zero time on stream.

Fig. 7 shows the product distribution with reaction time in the presence of K_2CO_3 , with other parameters unchanged. Figs. 6 and 7

Table 1
Product spectrum after 60 min of BPE conversion at 270 °C in the absence of carbonates.

Phenol [mol C%]	Benzyl alcohol [mol C%]	Toluene [mol C%]	Dimers [mol C%]	Trimers [mol C%]	Higher molecular weight compounds [mol C%]
18.8	21.3	0.21	4.1	0.6	18

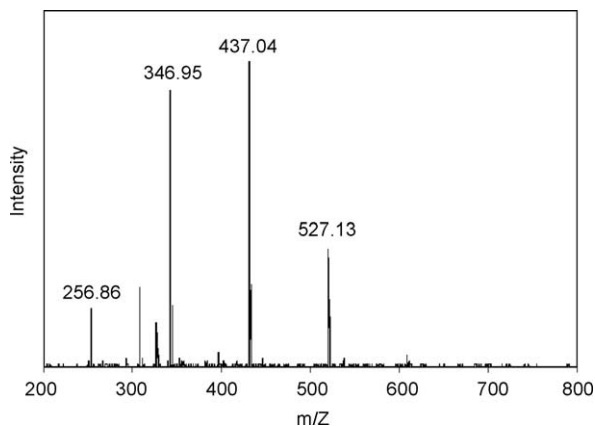


Fig. 4. LDI-TOF/MS spectrum of products obtained after 60 min at 300 °C.

illustrate the effect of the salt on the product distribution. While the yields of toluene, dimers and trimers were enhanced by the salt, the formation of the hydrolysis products phenol and benzyl alcohol was remarkably reduced. The ratios of the two hydrolysis products formed also diverge significantly. Assuming that phenol is formed only by hydrolysis, such results would indicate that at 320 °C, 50% of the initially produced benzyl alcohol has already been consumed in sequential reactions after 60 min. This is in line with the fact that benzyl alcohol is rather reactive compared to phenol. Therefore, it is suggested that lower temperatures, as well as shorter residence times, have to be applied, if high yields of primary hydrolysis products should be achieved.

Fig. 8 further supports this conclusion compiling the yields of phenol and benzyl alcohol with reaction time for the conversion of BPE with 3 wt% K_2CO_3 at 270–370 °C. The yields of benzyl alcohol and phenol are similar at 270 °C and both increased with prolonged reaction time up to 22 and 26%. At 320 °C yields of the two hydrolysis products were initially similar as seen from the extrapolation of the curves to zero time. With longer reaction time up to 60 min, both yields increased and reached a value of 21 and 42%. Afterwards, they decreased and became stable after another 60 min at average yields of 11 and 32% for benzyl alcohol and phenol, respectively. Increasing the reaction temperature to 350 °C accelerated the reaction to the extent that the benzyl alcohol was consumed within 5 min. A further increase to 370 °C yielded only 0.3% benzyl alcohol after 120 min. Thus, Fig. 8 not only shows the expected increase in reaction rate with increasing temperature, but also the instability of the hydrolysis products, especially benzyl alcohol, with increasing temperature.

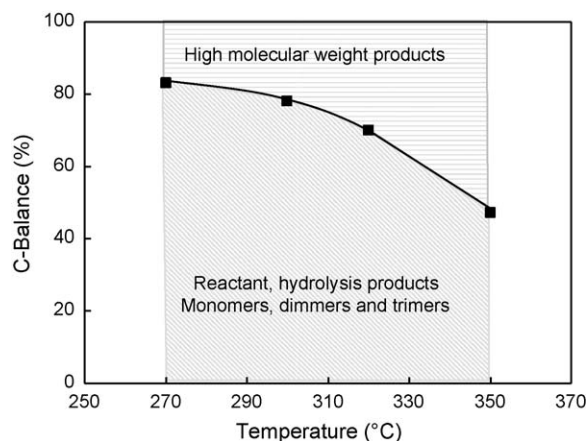


Fig. 5. Carbon balance and product distribution as a function of temperature for BPE conversion without adding alkali carbonates.

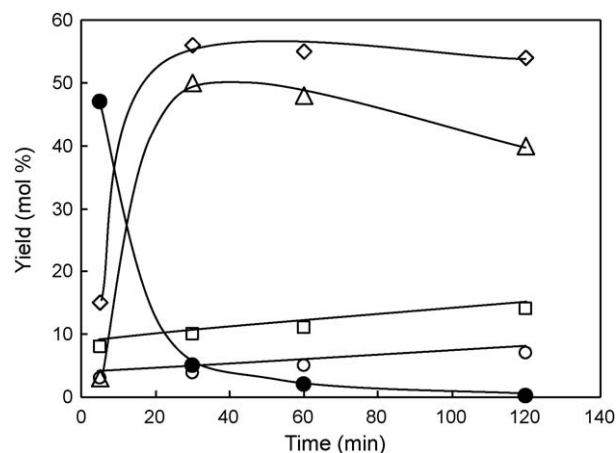


Fig. 6. Product distribution and unconverted BPE at 320 °C without adding alkali carbonate (●) BPE; (◇) phenol; (△) benzyl alcohol; (○) toluene; (□) secondary products.

For reasons of clarity, the yields of phenol and benzyl alcohol are combined as yield of hydrolysis products. Fig. 9 shows the effect of Li_2CO_3 , Na_2CO_3 or K_2CO_3 on the yields of hydrolysis products after 60 min at different temperatures. In each case, a maximum yield was reached between 300 and 320 °C. At 270 °C the carbonates showed a strong inhibiting effect on BPE hydrolysis, becoming less significant with decreasing CO_3^{2-} concentration and hence with decreasing basicity. At this temperature the yield is reduced from 80 to 18% in the presence of K_2CO_3 . In the case of Na_2CO_3 and Li_2CO_3 , yields have been even further decreased to 11 and 2%, respectively.

However, the inhibiting effect of the alkali carbonates decreases with temperature. After 60 min, the yield of hydrolysis product reached 81% in the case of Na_2CO_3 , while for K_2CO_3 and Li_2CO_3 , yield was 63 and 56%, respectively. In all cases, hydrolysis became less significant above 320 °C and yields of hydrolysis products approached approximately the same value for different carbonates.

4. Discussion

Depending on the reaction temperature and time, conversion of benzyl phenyl ether (BPE) in subcritical water leads to a broad but varying product distribution. In addition to the primary hydrolysis products, phenol and benzyl alcohol, large amounts of secondary products are formed. BPE is by far more reactive than diphenyl

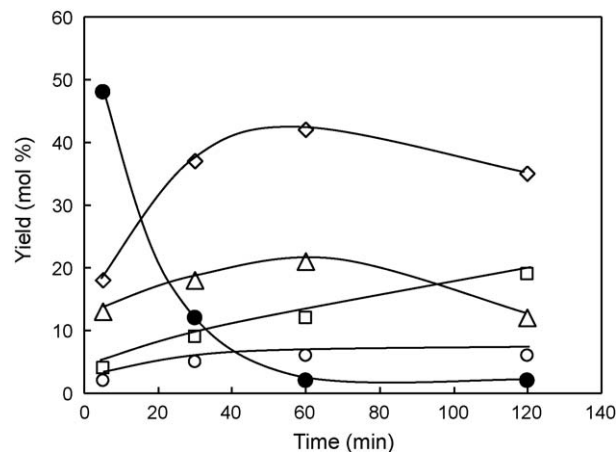


Fig. 7. Product distribution and unconverted BPE at 320 °C in the presence of 3 wt% K_2CO_3 (●) BPE; (◇) phenol; (△) benzyl alcohol; (○) toluene; (□) secondary products.

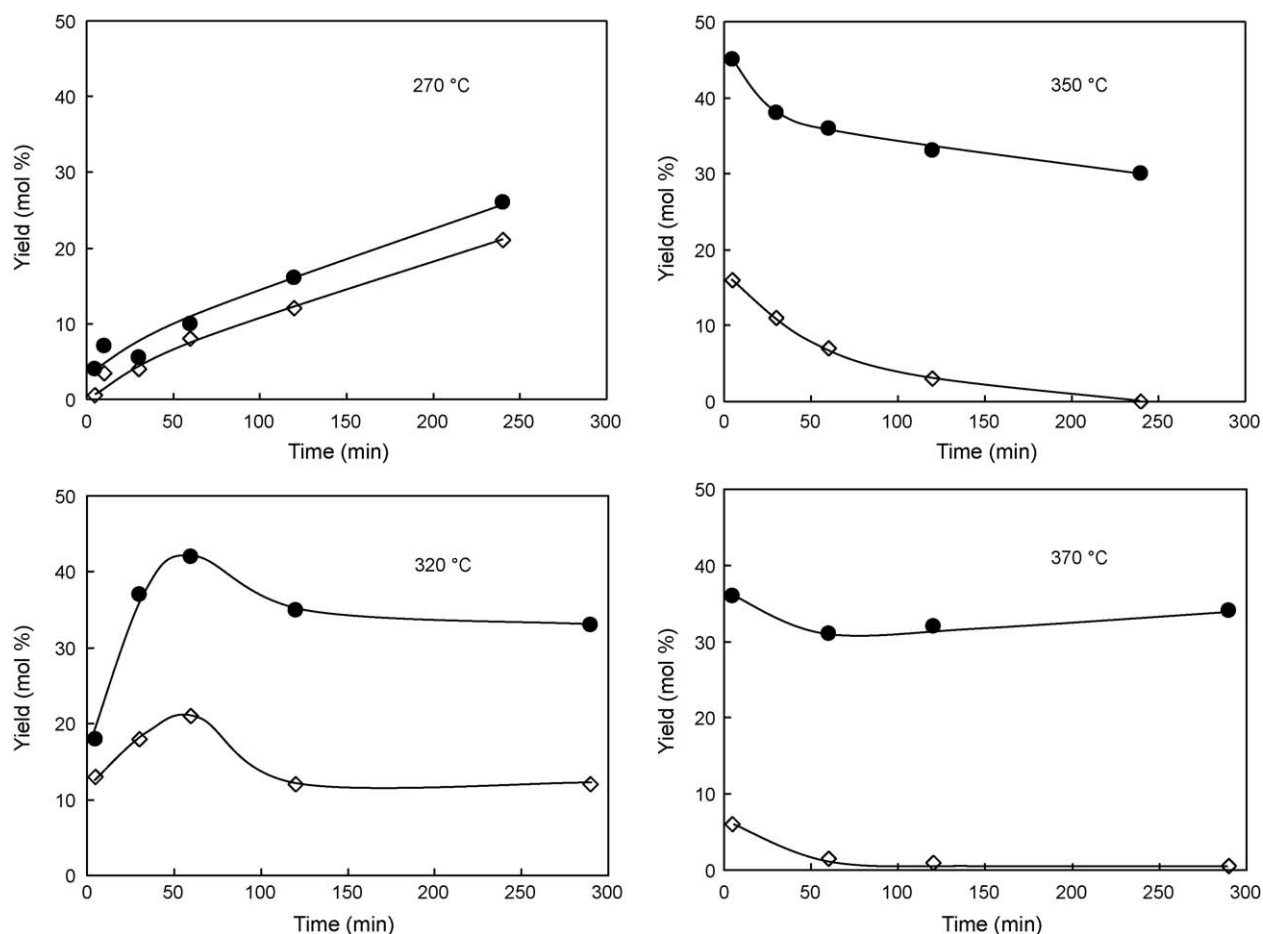


Fig. 8. Effect of reaction temperature and time on yield of hydrolysis products, (●) phenol and (◇) benzyl alcohol, with the addition of 3 wt.% K_2CO_3 .

ether, because the ether bond in BPE is less stable than the aryl-aryl ether bond [3]. The approximately 100 kJ/mol higher C–O bond energy in DPE results from the sp^2 hybridization of both carbon atoms involved.

At 270 °C the yields of consecutive products (dimers and trimers) were low (see Table 1). Only the primary hydrolysis products phenol and benzyl alcohol were formed in large quantities with an approximate ratio of 1 as expected for hydrolysis. The ionization constant of water, which determines the concentration of BPE hydrolysis catalyzing protons in the

system, reaches a maximum value around 250 °C. At these conditions, the ionization constant is three orders of magnitude higher than that at room temperature [13]. Therefore, it can be concluded that hydrolysis is the main reaction pathway at milder temperatures. The decrease of phenol and especially benzyl alcohol at higher temperatures and with reaction time results from the consecutive formation of dimers, trimers and even higher molecular weight compounds evidenced by LDI-TOF/MS measurements.

The high reactivity of benzyl alcohol under these conditions is well documented by the appearance of no less than 16 products ranging from toluene and benzaldehyde to dimers and trimers after reaction in water at 250 °C for 24 h [14]. However, as can be seen from the slopes in Figs. 6 and 7, the formation of toluene, 2- and 4-benzyl phenol, does not correspond to the decay of benzyl alcohol suggesting a direct BPE reaction pathway combined with a more complex chemistry. Thus, we conclude that toluene and 2- and 4-benzyl phenol are produced via a slower ionic pathway to be discussed in detail below.

In the presence of an alkali carbonate (exemplified in Figs. 3 and 7 for 3 wt.% K_2CO_3) two effects are notable. While, especially at lower temperatures, the overall rate of BPE conversion decreases in the presence of the salt, the primary hydrolysis products phenol and even more pronounced benzyl alcohol are formed with lower selectivity. To fully understand the effect of the alkali carbonate, the individual ions Me^+ and CO_3^{2-} must be observed separately as they have different effects on the reaction. The presence of the metal ion leads to the formation of a cation–BPE adduct, in which the ether bond is polarized and, therefore, more prone to be heterolytically cleaved. The carbonate neutralizes the protons

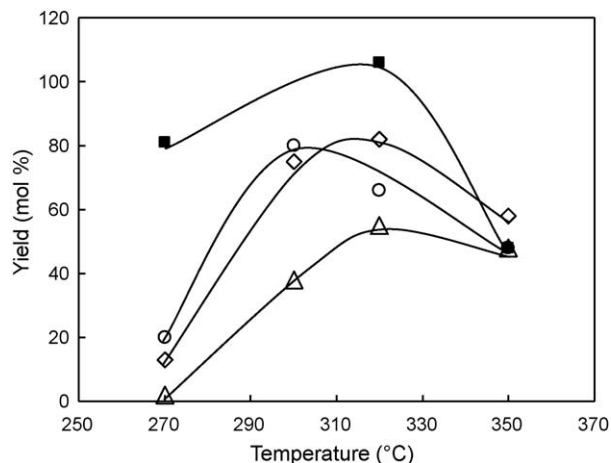


Fig. 9. Effect of temperature and carbonates, (■) no carbonate; (△) Li_2CO_3 ; (◇) Na_2CO_3 and (○) K_2CO_3 , on the yield of hydrolysis products (sum of phenol and benzyl alcohol) after 60 min reaction.

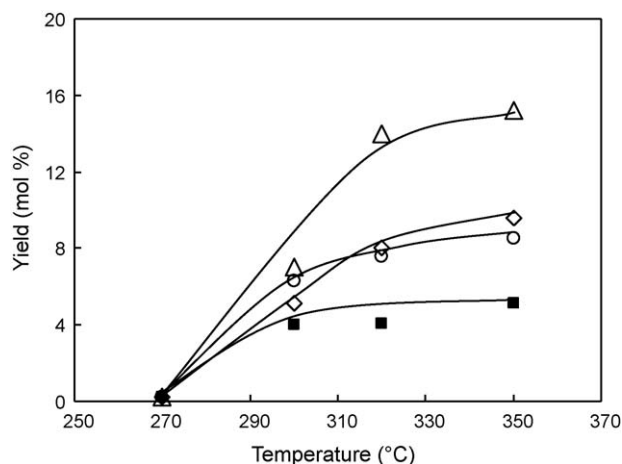


Fig. 10. Effect of temperature and carbonates, (■) no carbonate; (△) Li₂CO₃; (◇) Na₂CO₃ and (○) K₂CO₃, on the yield of toluene after 60 min reaction.

(catalyzing hydrolysis) leading so to a reduced BPE conversion. At higher temperatures the ionization constant of water is low and thus proton concentration is low. Therefore, the addition of carbonates only shows a small effect on hydrolysis at elevated temperatures. As example, see Fig. 9 in which the yield of hydrolysis products is not affected by alkali carbonates at 350 °C.

The decrease in hydrolysis selectivity in the presence of the salts is the direct result of the metal ion forming a cation–BPE adduct. In this formation, the ether bond is polarized and heterolytic cleavage and ionic attack are facilitated.

Further, a comparison of Figs. 6 and 7 also shows that phenol and especially benzyl alcohol are converted to secondary products much faster in the presence of an alkali carbonate. This shows that the addition of alkali carbonates does not only provide alternative ionic BPE conversion pathways, but also strongly enhances secondary reactions of the hydrolysis products phenol and benzyl alcohol.

Products formed via the mentioned alternative ionic reaction pathway are toluene, 2- and 4-benzyl phenol. As previously mentioned, the mechanism of formation for these products has been widely discussed in literature [4,6,8–10]. Our data however gives proof that these products are formed by an ionic mechanism, as we observe a strong effect of the alkali carbonate on the formation of these compounds. If the mechanism were to be of radical nature, a change in pH could potentially affect the selectivity of these products. However, the influence of alkali metal cation on toluene yield shown in Fig. 10 indicates that product formation is determined by the type of alkali metal cation. Note in this context that Li⁺ having the highest charge/radius ratio was the cation that enhanced toluene formation the strongest. In case of a homolytic cleavage, polarization by the cation should not affect the toluene yield. Therefore, we conclude that toluene is formed via an ionic mechanism (Fig. 11), induced by the polarization of the BPE ether bond by the cation. While this would certainly facilitate ionic cleavage of the ether bond, hydrogen transfer from another molecule must also be involved. As previously mentioned, Yokoyama et al. [4] reported that an

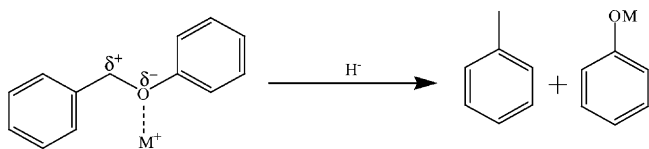


Fig. 11. BPE-cation adduct and concurrent ionic reaction pathways.

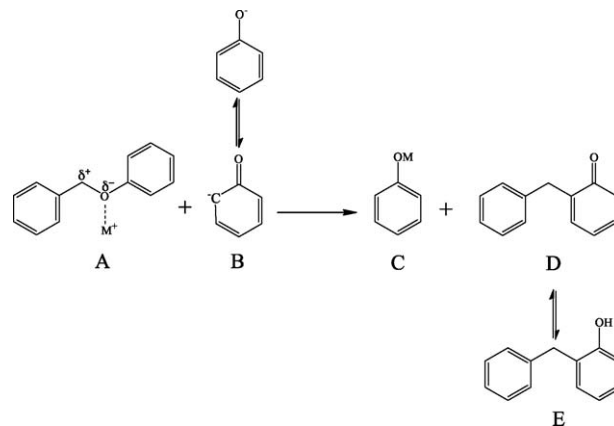


Fig. 12. Formation of 2-benzyl phenol via a carbanion.

increased density, e.g. by addition of a salt, can accelerate reactions such as hydrogen abstraction. It should also be noted that the relatively large fraction of high molecular weight compounds could likely serve as source of hydrogen.

The formation of a cation–BPE adduct is also concluded to be the cause for the formation of stable C–C bonds as in 2- and 4-benzyl phenol. As example, the formation of 2-benzyl phenol via an ionic pathway is shown in Fig. 12. As discussed above, the alkali cation interacts strongly with the oxygen of BPE. As a consequence, the ether bond is polarized and cleaves eventually heterolytically. The phenolate ion present in the alkaline media is stabilized by charge delocalization. Due to resonance stabilization, the phenolate ion also exists as a carbanion with a negative charge in ortho or para position of the phenolic hydroxyl group [15]. We propose that the carbanion (B) attacks BPE (A) at the polarized aliphatic C-atom forming a phenolate and 2-benzyl-cyclohexa-2, 4-dienone (D). Under the applied conditions, the ketone is more stable in its enol form and rearranges to 2-benzyl phenol (E).

5. Conclusions

The hydrolysis of BPE to phenol and benzyl alcohol reaches a maximum in the absence of an alkali carbonate and at temperatures at which the ionization constant of water reaches its highest value. Under these conditions, the concentration of protons catalyzing hydrolysis in the system formed by self dissociation of water is maximized. The decrease in temperature as well as the addition of alkali carbonate decreases the proton concentration leading to reduced hydrolysis. The presence of alkali carbonate, however, shows further effects on the secondary reactions of phenol and benzyl alcohol to high molecular compounds. The formation of the cation–BPE adduct strongly polarizes the ether bond making it easier to be cleaved heterolytically as we have shown for the formation of toluene and 2 and 4-benzyl phenol. Up to date, there has much debate if these products are formed via an ionic or a radical mechanism. It is shown here that the reaction proceeds via an ionic mechanism, which can be strongly affected by the addition of an alkali carbonate.

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